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PATENT KANTOOR
DEPARTEMENT VAN HANDEL
EN NYWERHEID



Certificate

REPUBLIC OF SOUTH AFRICA

PATENT OFFICE
DEPARTMENT OF TRADE AND
INDUSTRY

Hiermee word gesertifiseer dat
This is to certify that

REC'D 08 APR 2004
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the documents attached hereto are true copies of the Forms P2, P6,
provisional specification and drawings of South African Patent
Application No. 2003/1939 in the name of SASOL TECHNOLOGY
(PROPRIETARY) LIMITED

Filed : 10 March 2003

Entitled : Production of Linear Alkyl
Benzene

PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

Geteken te

PRETORIA

Signed at

in die Republiek van Suid-Afrika, hierdie

in the Republic of South Africa, this

16th

dag van

March 2004

day of

A stylized signature in cursive script, appearing to read "J. G. Goede".

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Registrar of Patents

REPUBLIC OF SOUTH AFRICA			REGISTER OF PATENTS			PATENTS ACT, 1978		
OFFICIAL APPLICATION			LODGING DATE: PROVISIONAL			ACCEPTANCE DATE		
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INTERNATIONAL CLASSIFICATION			LODGING DATE: COMPLETE			GRANTED DATE		
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FULL NAME(S) OF APPLICANT(S)/PATENTEE(S)								
71	SASOL TECHNOLOGY (PROPRIETARY) LIMITED							
APPLICANTS SUBSTITUTED:						DATE REGISTERED		
71								
ASSIGNEE(S)						DATE REGISTERED		
71								
FULL NAME(S) OF INVENTOR(S)								
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TITLE OF INVENTION								
54	PRODUCTION OF LINEAR ALKYL BENZENE							
ADDRESS OF APPLICANT(S)/PATENTEE(S)								
1 STURDEE AVENUE, ROSEBANK, 2196, GAUTENG, SOUTH AFRICA								
ADDRESS FOR SERVICE				S & F REF.				
74	SPOOR & FISHER, SANDTON			PA134867/P				
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APPLICATION FOR A PATENT

AND ACKNOWLEDGEMENT OF RECEIPT 03.03
(Section 30 (1) – Regulation 23)

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The granting of a patent is hereby requested by the undermentioned applicant on the basis of the present application filed in duplicate

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OFFICIAL APPLICATION NO.

21 01

2003/1939

PA134867/P

FULL NAME(S) OF APPLICANT(S)

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CORRECTIONS
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TITLE OF INVENTION

54

PRODUCTION OF LINEAR ALKYL BENZENE

THE APPLICANT CLAIMS PRIORITY AS SET OUT ON THE ACCOMPANYING FORM P.2. THE EARLIEST PRIORITY CLAIM IS:

COUNTRY: NIL

NUMBER: NIL

DATE: NIL

THIS APPLICATION IS FOR A PATENT OF ADDITION TO PATENT APPLICATION NO.

21 01

THIS APPLICATION IS A FRESH APPLICATION IN TERMS OF SECTION 37 AND IS BASED ON APPLICATION NO.

21 01

THIS APPLICATION IS ACCCOMPANIED BY:

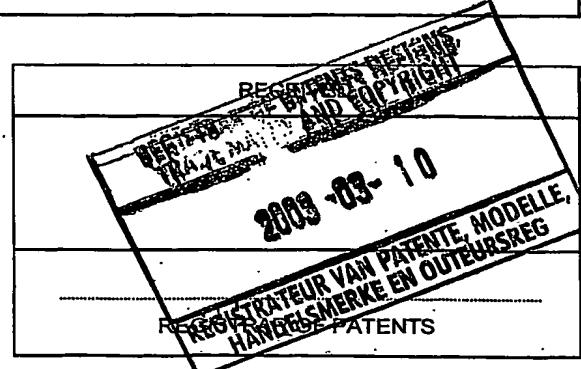
- 1. A single copy of a provisional specification of 9 pages.
- 2. Drawings of 2 sheets.
- 3. Publication particulars and abstract (Form P.8 in duplicate).
- 4. A copy of Figure of the drawings (if any) for the abstract.
- 5. Assignment of invention.
- 6. Certified priority document.
- 7. Translation of the priority document.
- 8. Assignment of priority rights.
- 9. A copy of the Form P.2 and the specification of S.A. Patent Application No .
- 10. Declaration and power of attorney on Form P.3.
- 11. Request for ante-dating on Form P.4.
- 12. Request for classification on Form P.9.
- 13. Form P.2 in duplicate.
- 14. Other.

74 ADDRESS FOR SERVICE: SPOOR & FISHER, SANDTON

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SPOOR & FISHER
PATENT ATTORNEYS FOR THE APPLICANT(S)



REPUBLIC OF SOUTH AFRICA
PATENTS ACT, 1978

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DESMET, MIEKE ANN

TITLE OF INVENTION

54 | PRODUCTION OF LINEAR ALKYL BENZENE

PRODUCTION OF LINEAR ALKYL BENZENE

BACKGROUND OF THE INVENTION

THIS invention relates to a method for producing linear alkyl benzene.

Alkyl benzene derivatives, such as alkyl benzene sulphonates, are among others, used in detergent and surfactant product applications. Environmental legislation requires that these products are biodegradable. It is well known that, to be bio-degradable, it is important for the alkyl chain to be linear, i.e. with very little or no branching and low, if any, quaternary carbons.

In conventional processes for producing linear alkyl benzenes, a hydrocarbon stream is hydrogenated in order to convert oxygenates and olefin species in the stream to paraffins. Hydrogenation also allows for the removal of sulphur and nitrogen contaminants that may be present. Following the hydrogenation reaction, the resulting paraffin stream is fractionated into various carbon ranges. A carbon range, for example the C₈ to C₁₆ range, which includes branched paraffins, is passed through a molecular sieve. The branched paraffins are rejected as a raffinate stream, whilst the linear paraffins are passed through a dehydrogenation reactor to form an olefin/paraffin mixture. This mixture is then fed to an alkylation plant and reacted with benzene to form linear alkyl benzene (LAB). The linear alkyl benzene is then sulphonated to form linear alkyl benzene sulphonates (LAS). A problem with this approach is the relatively high cost of paraffinic starting material and the high cost associated with the production of linear paraffins from kerosene feedstocks.

United Kingdom Patent No. 669,313 in the name of California Research Corporation, United States Patent No. 3,674,885 in the name of Atlantic Richfield Company and International Patent Publication No. WO 01/64610 in the name of Chevron USA Inc. disclose the use of a hydrocarbon condensate from the Fischer-Tropsch process, in the production of alkyl benzene. These references disclose that the hydrocarbon condensate contains olefins which are used in the alkylation reaction to form linear alkyl benzene. These references are limited to the use of "high temperature" Fischer-Tropsch processes wherein the Fischer-Tropsch reaction is carried out temperatures of approximately 300°C and higher, and the preferred catalysts are iron-containing catalysts, for the production of the hydrocarbon condensate. The high temperature Fischer-Tropsch processes were found to be suitable because the hydrocarbon condensate contains a high concentration of olefins, usually in the region of around 70%. Although these references refer to linear olefins, in practice the olefins obtained from a high temperature Fischer Tropsch process exhibit more than 10 % branching.

SUMMARY OF THE INVENTION

According to the invention there is provided a method for producing linear alkyl benzene, the method including the steps of obtaining a hydrocarbon condensate containing olefins and paraffins from a low temperature Fischer-Tropsch reaction;

- a) fractionating a desired carbon number distribution from the hydrocarbon condensate to form a fractionated hydrocarbon condensate;
- b) extracting oxygenates from the fractionated hydrocarbon condensate;
- c) alkylating the hydrocarbon condensate with benzene in the presence of a suitable alkylation catalyst; and
- d) recovering linear alkyl benzene and paraffin.

Typically, the low temperature Fischer-Tropsch reaction is carried out at a temperature of 160°C - 280°C, preferably 210°C - 260°C, and preferably in the presence of a cobalt catalyst to provide a hydrocarbon condensation product containing 60 to 80% by weight paraffins and 10 to 30% by weight, typically less than 25% by weight, olefins. The olefins so produced having a high degree of linearity of greater than 92%, preferably greater than 95%.

The hydrocarbon condensate product is fractionated into the C₈ to C₁₆ range, preferably into the C₁₀ to C₁₃ range.

The oxygenates may be extracted by distillation, liquid-liquid extraction or dehydration, preferably liquid-liquid extraction. A light solvent such as dry methanol or a mixture of methanol and water, is preferably used in the liquid-liquid extraction.

This invention specifically relates to a hydrocarbon condensate product from a low temperature Fischer-Tropsch reaction in the C₁₀ to C₁₃ range containing 15 to 30%, typically less than 25%, by weight olefins with a high degree of linearity of greater than 92%, typically greater than 95%, suitable for use in a process for manufacturing linear alkyl benzene.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a block diagram of a process according to the invention for producing linear alkyl benzene; and

Figure 2 is a block diagram of a process for extracting oxygenates from a hydrocarbon product; used in the process of Figure 1.

DESCRIPTION OF PREFERRED EMBODIMENTS

This invention relates to the use of a hydrocarbon condensate stream from a low temperature Fischer-Tropsch reaction in the production of linear alkyl benzene.

In the Fischer-Tropsch process, synthesis gas (carbon monoxide and hydrogen) obtained from gasification of coal or reforming of natural gas, is reacted over a Fischer Tropsch catalyst to produce a mixture of hydrocarbons ranging from methane to waxes and smaller amounts of oxygenates.

In a low temperature Fischer-Tropsch reaction, the reaction takes place in a slurry bed reactor or fixed bed reactor, preferably a slurry bed reactor, at a temperature in the range of 160°C - 280°C, preferably 210°C - 260°C, and a pressure in the range of 18-50 bar, preferably between 20-30 bar, in the presence of a catalyst. The catalyst may include iron, cobalt, nickel or ruthenium. However, a cobalt-based catalyst is preferred for the low temperature reaction. Usually, the cobalt catalyst is supported on an alumina support.

During the Fischer-Tropsch reaction, a lighter hydrocarbon vapour phase is separated from a liquid phase comprising heavier liquid hydrocarbon products. The heavier liquid hydrocarbon product (waxy products) is the major product of the reaction and may, for example, be hyrocracked to produce diesel and naphtha.

The lighter hydrocarbon vapour phase which comprises gaseous hydrocarbon products, unreacted synthesis gas and water is condensed to provide a "condensation product" which comprises an aqueous phase and a hydrocarbon condensation product phase.

The hydrocarbon condensation product includes olefins and paraffins in the C₄ to C₂₈ range, and oxygenates including alcohols, esters, aldehydes, ketones and, acids.

Olefins, which are predominantly alpha olefins, only make up approximately 15% to 30%, typically less than 25%, by weight, of the hydrocarbon condensation product. Generally, this product would not be considered useful in an alkylation reaction to form linear alkyl benzene, because of the low concentration of olefins. However, it has been found that the olefins in the low temperature Fischer-Tropsch hydrocarbon condensate product have a very high degree of linearity of greater than 95% and, even though they only make up 15 to 30% typically less than 25%, by weight of the hydrocarbon condensate product, it is an excellent feed for the production of linear alkyl benzene and provides an economically viable manner for the production of highly linear alkyl benzene.

The hydrocarbon condensation product includes 60% to 80% by weight paraffins which have a linearity of greater than 92%, and 5% to 10% by weight oxygenates.

Referring to Figure 1, by way of example, a hydrocarbon condensate product 10 from a low temperature Fischer-Tropsch reaction contains 20% by weight olefins, 74% by weight paraffins, and 6% by weight oxygenates. The hydrocarbon condensate product 10 is passed through a fractionation column 12 and a C₁₀-C₁₃ cut 14 is separated therefrom. The cut 14 contains 22% by weight olefins, 71% by weight paraffins and 7% by weight oxygenates. The cut 14 is then sent to an oxygenate removal unit 16 where the oxygenates 18 are removed to provide a hydrocarbon feed stream 24 containing 23% by weight olefins and 77% by weight paraffins and less than 0.01% by weight oxygenates.

As mentioned above, the olefin concentration in the cut 14 is low. It is therefore desirable to use an oxygenate removal step which preserves the olefin concentration. In the prior art, many methods of removing

oxygenates from hydrocarbon streams are suggested. Such removal methods include hydrogenation, azeotropic distillation, extractive distillation; vapour phase dehydration, liquid phase dehydration and liquid-liquid extraction. Distillation, liquid-liquid extraction and dehydration processes are preferred as they tend to preserve the olefin concentration.

With reference to figure 2, a liquid-liquid extraction process of the invention includes an extraction column 20. The cut 14 from Figure 1 is fed into the extraction column 20 at or near the bottom thereof and a solvent stream 21 is fed into the extraction column 20 at or near the top thereof.

Raffinate 22 from the top of the extraction column 20, which includes olefins and paraffins and a small amount of solvent, enters a raffinate stripper column 23 and a hydrocarbon feed stream containing olefins (23% by weight), and paraffins (77% by weight) and less than 0.01% by weight oxygenates exits as a bottoms product 24 while solvent exits as a tops product 25 and is returned to the solvent feed stream 21. If it is desired to recover the bottoms product 24 as a vapour stream, this can be done by adding a vapour side draw to the column just above the reboiler. The liquid product from the reboiler will then be a very small effluent stream.

An extract 26 is drawn from the bottom of the extraction column 20 and is fed to solvent recovery column 27. Oxygenates exit as a bottoms product 28 from the solvent recovery column 27, while solvent exits as a tops product 29 and is recycled to the solvent stream 21. The oxygenate content of the tops product 29 can be as low as 50 ppm, depending on the solvent to feed ratio used in the extraction column 20.

The solvent 21 can be any polar material that has partial miscibility with the feed stream 14, such as tri-ethanol amine, tri-ethylene glycol with between zero and 20% water, acetonitrile with between 5% and 20% water, acetol, diols, methanol, or ethanol and water. A combination of the above solvents is also possible.

Normally, a high-boiling solvent is preferred for liquid-liquid extraction because the solvent recovery steps after extraction requires less energy than will be the case for a low-boiling solvent. However, it has been found that dry methanol, or a mixture of methanol and water, which is a low-boiling solvent, need not suffer from this drawback, because it can be effective at low solvent to feed ratios (this can be lower than 1:1 if the required oxygenate removal is not too severe).

A study of the different azeotropes that exist between components in the feed and methanol and water would lead one to expect that it would not be possible to distil water overhead in the solvent recovery column 27 without azeotroping oxygenates overhead as well. Surprisingly, this turns out not to be the case. Methanol, which does not form azeotropes with any of the other species present, prevents the water/oxygenate azeotropes from distilling over at the same temperature as the paraffins and olefins. This appears to be due to an extractive distillation effect. Additionally, it is possible to distil the paraffins and olefins overhead, while recovering all the oxygenates as bottom products (this is not possible for a dry methanol system, because only a fraction of the paraffins and olefins can be distilled overhead without carrying over oxygenates in a dry methanol system). This has the effect of enhancing the overall paraffin and olefin recovery of the process, because the overheads 29 of the solvent recovery column 27 is recirculated to the extraction column 20, which means that the paraffins and olefins will be forced to leave the process in the product stream 24. It is therefore possible to have a pure hydrocarbon (paraffin and olefin) stream 24, and a pure oxygenate and water stream 28 as products from the process, without the use of a countercurrent in the extraction column. In this mode of operation, all the methanol, and part of the water (10-50%) are also recovered in the overhead stream 29.

Because the bottoms product 28 contains a high percentage of water (10-60%), this stream will form two liquid phases that can be decanted in a decanter 30. The organic phase will be a pure oxygenate stream 31, which leaves the process as a product. The aqueous phase will be a stream 32,

which can be recycled to the extraction column 20. This stream can either enter the extraction column at the top along with the solvent stream 21, or slightly lower down the column 20, to prevent the low amount of oxygenates that will be present in this stream from appearing in the raffinate stream 22.

It is also possible to run the extraction column 20 and the solvent recovery column 27 at different methanol / water ratios. This may be desirable because a high water content in the extraction column 20 will lead to increased solvent to feed ratios (because of reduced solubility of oxygenates in the solvent); while a certain amount of water is necessary to achieve the extractive distillation effect in combination with methanol to recover all the paraffins and olefins as overhead products in the solvent recovery column 27. The different methanol / water ratios in the two columns (20 and 27) can be achieved by diverting some of the water in stream 32 to stream 26 by means of a stream 33.

Referring back to Figure 1, according to the invention, the liquid hydrocarbon product 24 from the oxygenate removal process 16 is introduced into an alkylation reactor 40. The alkylation reaction may be carried out by using a Friedel-Crafts type condensation catalyst such as AlCl_3 , H_2SO_4 , BF_3 , HF or a solid acid catalyst. In the present case, UOP's DETAL solid-acid catalyst alkylation technology is used. Typically, the alkylation reaction is carried at temperatures of approximately 100°C and pressures of about 300kPa (abs) in the presence of UOP's proprietary DETAL catalyst. (see Smith R. (1991). Linear alkyl benzene by heterogeneous catalysis, PEP Review No. 90-2-4, SRI International). In this process, benzene 42 and the olefin component of the liquid hydrocarbon product 24 are reacted in the alkylation reactor 40 using a solid acid catalyst to produce highly linear alkyl benzene 44. Heavy alkylates 46 and paraffins 48 are removed. The paraffins 48, which do not react in the reactor, are of a very high quality and may be sold or may be used in further process, for example they may be hydrogenated and used in a

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conventional process for producing linear alkyl benzene. Benzene 50 is recovered and recycled to the alkylation reactor.

The highly linear alkyl benzene 44 is then introduced to a sulphonation reactor 52 and sulphonated using sulphuric acid, oleum or sulphur trioxide. Sulphur trioxide is currently the preferred process. The sulphonation process results in the formation of a highly linear alkylbenzene sulphonates 54.

The process of the invention makes use of a feed stream in the form of a condensate product from a low temperature Fischer-Tropsch reaction which would not, ordinarily, be thought of for producing linear alkyl benzene. The process produces a desirable highly linear alkyl benzene product, while at the same time produces a high quality paraffin product which may be sold or used in further processes, making the process economically viable. To give an example, of the total global C₈ - C₁₆ paraffin demand most of the demand is for the C₁₀ - C₁₃ fraction, which is used predominantly for LAB production, detergent alcohol production and miscellaneous industrial uses.

Dated this 10TH day of March 2003

Spoor & Fisher
Applicant's Patent Attorneys

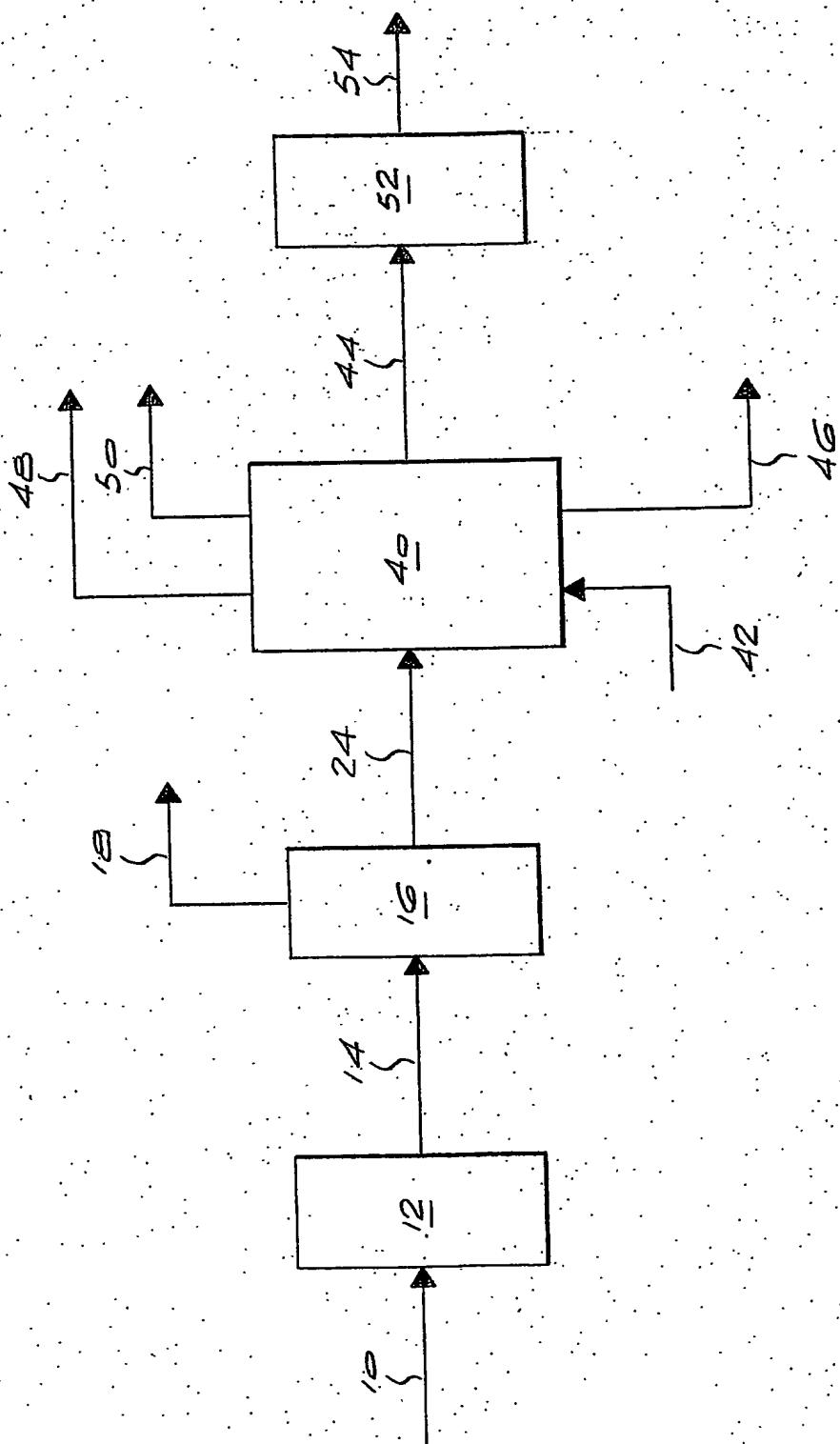
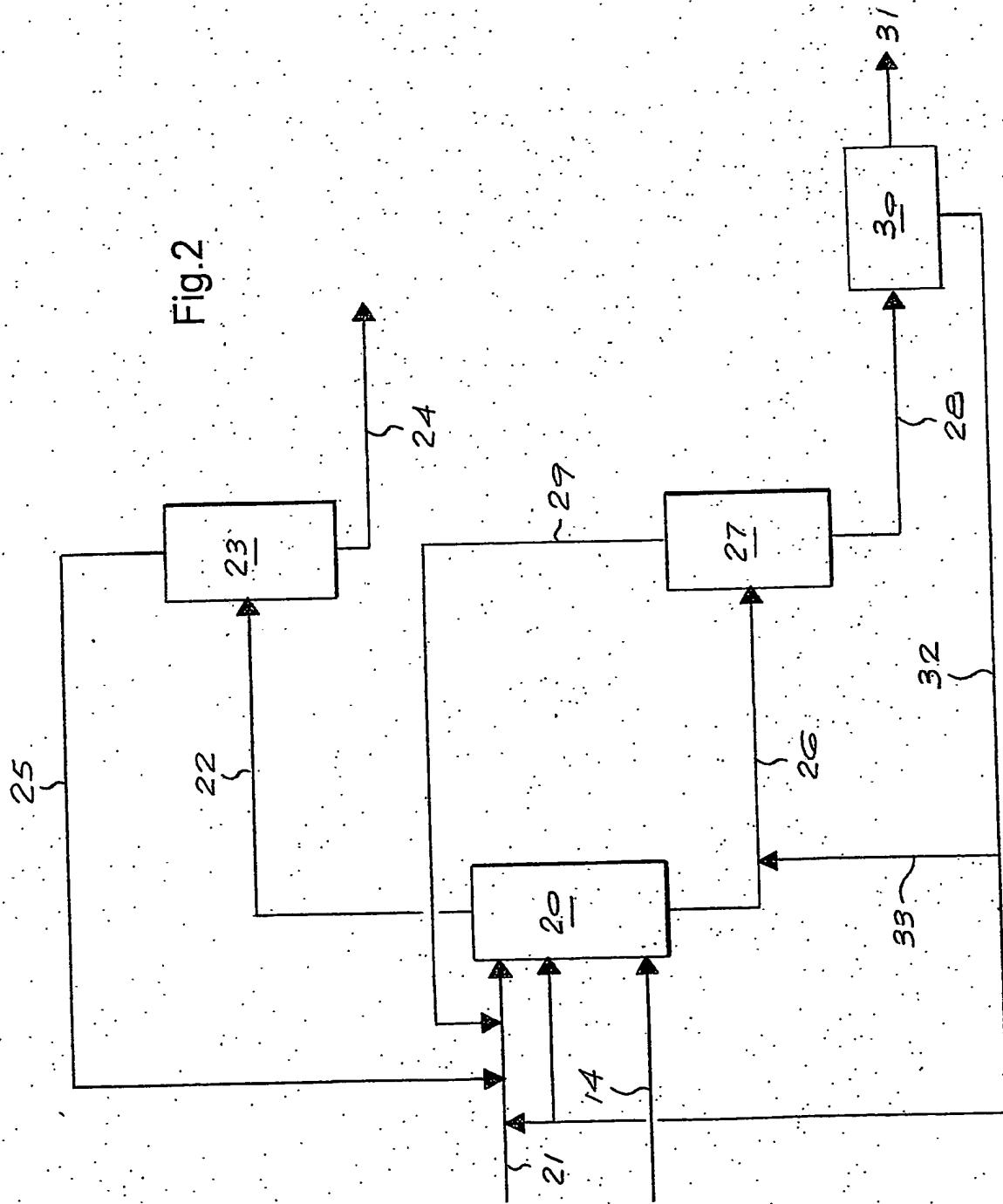


Fig. 1

Fig.2



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SPOOR & FISHER